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THE FIRST ORGANOGALLIUM FOUR-MEMBERED RING COMPOUND WITH ARSENIC, HALOGEN MIXED BRIDGING: SYNTHESIS AND CRYSTAL STRUCTURE OF $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$

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Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, NC 27706, U.S.A.

Abstract $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ (1) has been isolated from the products of the room temperature reaction of Ph_2GaCl with $(Me_3Si)_3As$ (reactants mixed in both a 2:1 and a 3:1 mole ratio). A mixture of 1 and $[Ph_2GaAs(SiMe_3)_2]_2$ (2) was isolated after heating a 1:1 mole ratio combination of the same reactants. Reaction of pure 2 [prepared from Ph_2GaCl and $LiAs(SiMe_3)_2$] with Ph_2GaCl resulted in the formation of (1). Prolonged heating of 1 produced a mixture of 2, Me_3SiCl and unidentified products. Compound 1 was structurally characterized by a single crystal X-ray analysis and shown to be the first organogallium four-membered ring compound with both an arsenic and a halogen bridge. The ring of 1 is clearly non-planar as evidenced by the fact that the Cl atom is displaced from the Ga-As-Ga' plane to yield a dihedral angle of 8.8° between the Ga-As-Ga' and Ga-Cl-Ga' planes. Various other features of the structure of 1 are discussed.

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Prepared for Presentation at the Fifth International Symposium on Inorganic Ring Systems and for Publication in Phosphorus and Sulfur

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Department of Chemistry
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August 3, 1988

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INTRODUCTION

In gallium chemistry, four-membered ring formation is known to occur via bridging of gallium centers by two arsenic atoms[1] or two halogen atoms[2], but the literature contains no references to this occurring through one of each of these atoms. Here we report the synthesis and crystal structure of $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ (1), the first organogallium four-membered ring compound resulting from arsenic, halogen mixed bridging. We also report the synthesis of $[Ph_2GaAs(SiMe_3)_2]_2$ (2). The fact that **1** can be prepared from Ph_2GaCl and $(Me_3Si)_3As$ again exemplifies the utility of

dehalosilylation between a silylarsine and a halogallane in preparing novel gallium-arsenic systems.[1,3]

RESULTS AND DISCUSSION

Combining C_6H_6 solutions of Ph_2GaCl[4] and $(Me_3Si)_3As$[5] (2:1 mole ratio), followed by stirring at room temperature and removal of solvent and Me_3SiCl, gave a white solid. A ligroin extract of the solid afforded **1** as white crystals [mp 145-146 °C (dec), 55.3% yield]. A satisfactory molecular weight was obtained by cryoscopic measurements. NMR: $^{13}C\{^1H\}$ (C_6D_6) δ 3.14 (s, Me_3Si), 128.30, 128.72, 135.81, 146.57 (m, Ph).

$$2Ph_2GaCl + (Me_3Si)_3As \rightarrow \underset{\mathbf{1}}{Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2}Cl} + Me_3SiCl$$

Likewise, mixing solutions of Ph_2GaCl and $(Me_3Si)_3As$ (3:1 mole ratio) resulted in the formation of **1** as the predominant product (53.5% yield).

A mixture of **1** and **2**, Me_3SiCl and other unidentified products were isolated after heating (76 °C) a 1:1 mole ratio combination of Ph_2GaCl and $(Me_3Si)_3As$ in C_6H_6. Compounds **1** and **2** were identified as the components of the mixture by comparison of the $^{13}C\{^1H\}$ NMR spectrum of the mixture with those of authentic samples of **1** and **2**. The latter was prepared from Ph_2GaCl and $LiAs(SiMe_3)_2$[5] (1:1 mole ratio) in benzene and isolated as white crystals [mp 229-230 °C (dec), 33.3% yield], and it was determined to be a dimer in solution by cryoscopic molecular weight measurements. NMR: $^{13}C\{^1H\}$ (C_6D_6) δ 4.82 (s, Me_3Si), 127.75, 128.02, 137.62, 149.55 (m, Ph).

$$Ph_2GaCl + LiAs(SiMe_3)_2 \rightarrow \underset{\mathbf{2}}{1/2[Ph_2GaAs(SiMe_3)_2]_2} + LiCl$$

The production of **1** was also accomplished by allowing Ph_2GaCl and **2** (2:1 mole ratio in C_6D_6) to react in a sealed NMR tube.

RING COMPOUND WITH ARSENIC, HALOGEN MIXED BRIDGING

Heating a sample of **1** in C_6D_6 in a sealed NMR tube for one month at 80 °C resulted in the formation of **2**, Me_3SiCl and other unidentified products.

An X-ray crystal structure analysis of **1** revealed that the asymmetric unit comprises a discrete molecule (Figure 1) containing the heretofore unknown As- and Cl-bridged four-membered Ga-As-Ga'-Cl ring. That this ring is not strictly planar, and thus

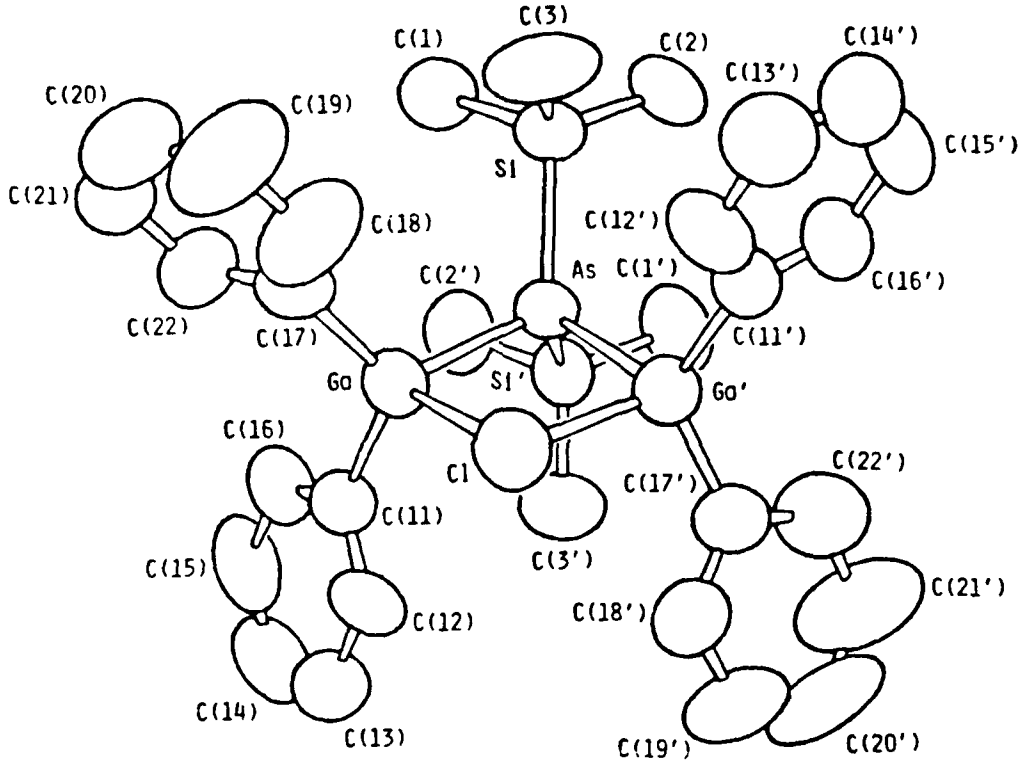

FIGURE 1 Molecular structure of $Ph_2\overline{GaAs(SiMe_3)_2Ga(Ph)_2Cl}$ (**1**) (hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Ga-As 2.469(2), Ga'-As 2.463(2), Ga-Cl 2.412(3), Ga'-Cl 2.409(4), Si-As 2.359(4), Si'-As 2.367(4), Ga-As-Ga' 88.70(7), Ga-Cl-Ga' 91.3(1), As-Ga-Cl 89.5(1), As-Ga'-Cl 89.8(1), Si-As-Si' 111.0(2), C(11)-Ga-C(17) 120.0(5), C(11')-Ga'-C(17') 122.6(5).

the molecule deviates from exact $\underline{C_{2v}}$ symmetry presumably to relieve unfavorable non-bonded intramolecular interactions between substituents in such a symmetric form, is manifested by the Cl atom displacement of 0.256 Å from the Ga-As-Ga' plane (the associated angle between the Ga-As-Ga' and Ga-Cl-Ga' planes is 8.8° and the mean endocyclic dihedral angle about the ring bonds is 6.2°). The extent of the departure from exact planarity in **1** is somewhat less than in the $(Ga\text{-}As)_2$ ring of $\{[(Me_3SiCH_2)_2As]_3Ga\}_2$[6] where more severe overcrowding of the bulkier ring substituents leads to corresponding interplanar and dihedral angles of 13.6° and 10.2°, respectively. In contrast to the situation in $(Ga\text{-}As)_2$ rings where the endocyclic angles subtended at As and Ga differ significantly [range: 94.57(4) - 96.02(4)° and 83.58(4) - 85.02(2)°, respectively],[1] those in **1** are almost equal [88.70(7)° at As; 89.5(1) and 89.8(1)° at Ga]. The bond angle at the bridging Cl atom [91.3(1)°] is nearly the same as that of 91.4(1)° in $[Ga(C_5H_5)Cl_2]_2$ (**3**)[7] and lies in the middle of the range of 86(2)° in $(GaCl_3)_2$ (**4**)[8] and the mean of 97.4(2)° in $[Ga(C_5Me_5)_2Cl]_2$ (**5**).[7] The mean C-Ga-C angle at 121.3(5)° is close to the corresponding value of 120.8(2)° in $[(Me_3SiCH_2)_2AsGaPh_2]_2$.[9] A significantly larger Si-As-Si' angle [111.0(2)°] is present in **1** than in $[(Me_3Si)_2AsLi{\bullet}DME]_2$ (DME = 1, 2-dimethoxyethane) (**6**) [103.2(4)°].[10] The mean Ga-As bond length in **1** [2.466(2) Å] is shorter than any found within $(Ga\text{-}As)_2$ rings [range: 2.513(1) - 2.581(1) Å],[1] whereas the mean Ga-Cl distance at 2.411(4) Å is longer than the corresponding length in **4** [2.29(9) Å] as well as the mean of those in **3** [2.363(3) Å], but it is shorter than the mean in **5** [2.448(7) Å]. The mean Si-As distance at 2.363(4) Å is significantly longer than in **6** [2.307(7) Å].

Finally, the ^{13}C NMR spectrum and the experimentally determined molecular weight of **1** indicate it has the same molecular structure in solution as in the solid state.

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